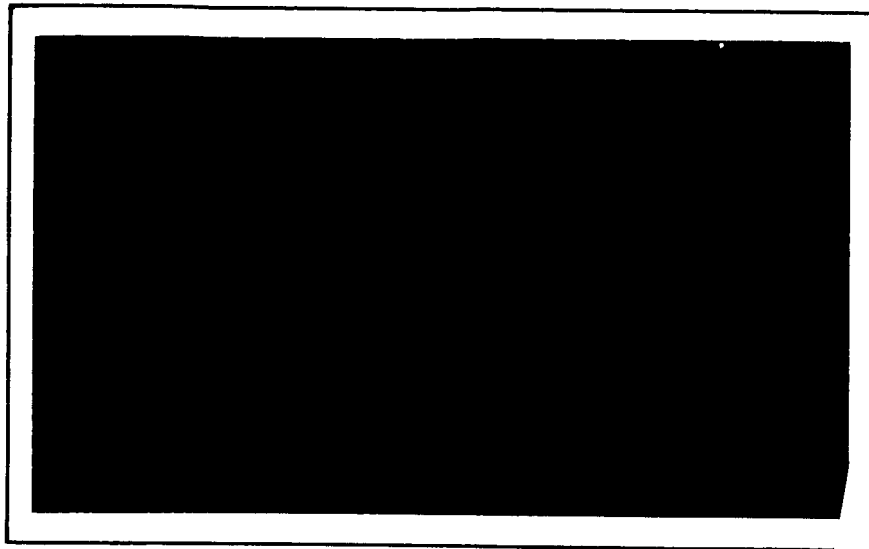


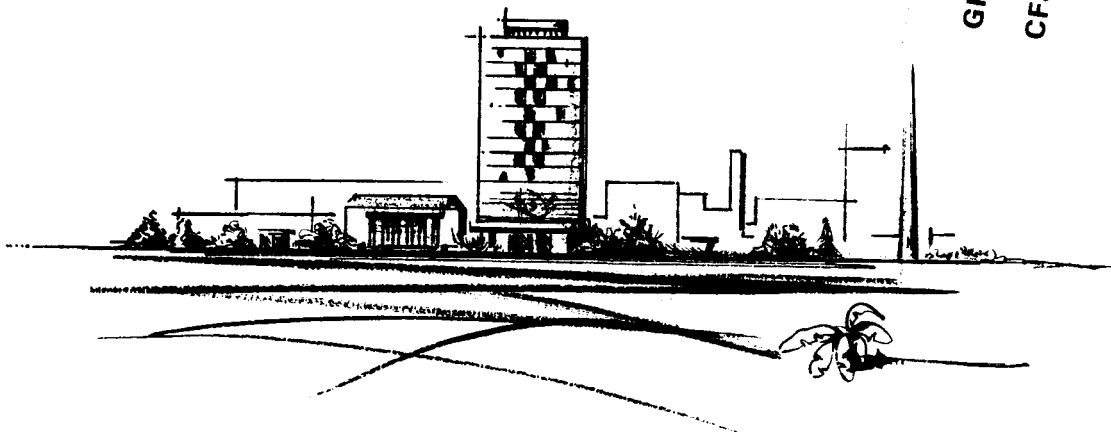
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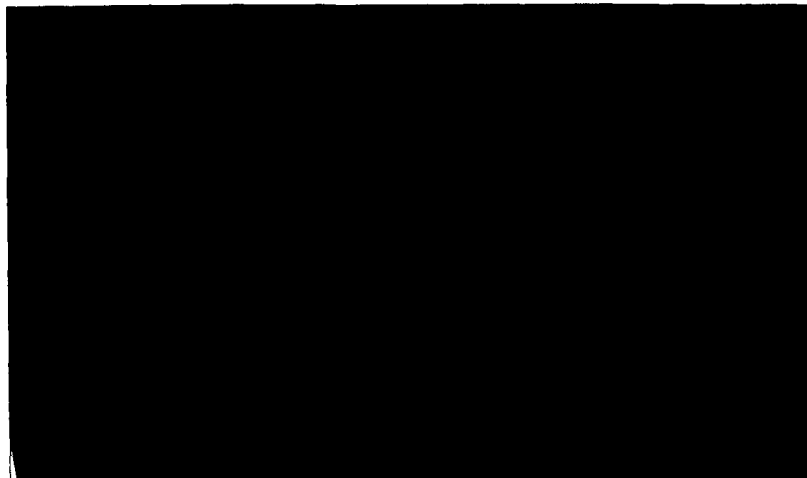
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FINAL TECHNICAL REPORT

on

A STUDY OF SOLID-PROPELLANT
VAPORIZATION AND DIFFUSION PROCESSES

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

August 31, 1965

by

J. W. Droege, R. W. King, J. S. McNulty, and A. Levy

Contract No. 950813

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A STUDY OF SOLID-PROPELLANT VAPORIZATION AND DIFFUSION PROCESSES

by

J. W. Droege, R. W. King, J. S. McNulty, and A. Levy

SUMMARY

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Composite solid propellants are relatively stable during prolonged exposure to the vacuum of space. The major components are nonvolatile and therefore not subject to loss by evaporation. Certain components, present in small amounts, may be lost by evaporation, with the possible result of a serious deterioration of the properties of the propellant. In this program, the vaporization and diffusion processes for dioctyl adipate and ferrocene in a polyurethane propellant were studied in some detail; phenyl-beta-naphthylamine was studied in less detail.

Vapor pressures of these three additives were measured, using both the Knudsen and the Langmuir techniques. Diffusion studies were carried out on propellant samples containing dioctyl adipate and ferrocene. Measurements were made between 30 and 70°C. The diffusion coefficients found for these two materials were nearly the same. The vapor pressures differed by several orders of magnitude.

Diffusion appeared to take place predominantly through the polymer phase. There were some indications of structure-dependent diffusion through cracks and boundaries between the binder and the oxidizer.

If one assumes a rocket configuration in which the effective throat area is about 3×10^{-3} times the area of exposed propellant surface, then one concludes that at about 30°C the loss of dioctyl adipate will be controlled by its rate of effusion from the nozzle. Over a period of a few years, the loss would be negligible. For ferrocene, with a much higher vapor pressure, the loss is diffusion controlled and in a year would deplete the propellant considerably within a few millimeters of the surface, leaving the bulk of the propellant unaffected.

Author

INTRODUCTION

The composition of a solid propellant used in today's rockets is carefully selected, together with the motor design, to achieve a desired performance. The physical properties of the propellant must be such that the integrity of the grain will be preserved up to and through the time of its use. Likewise, the burning characteristics, e. g., ignitability and burning rate, must be preserved and must operate as predicted, after some period of time in space. Extended terrestrial storage and shelf-life studies have been carried out to insure that the important mechanical and burning properties of the propellant do not deteriorate with time. For certain purposes, however, it will be required

that some solid-filled motors survive extensive storage in space. These space-storage conditions differ from terrestrial storage conditions in three significant ways - the absence of gravity, the virtual absence of atmosphere, and the presence of a high radiation field. The first of these is considered to be of little significance with respect to space storage of solid propellants. High-vacuum and radiation environments, on the other hand, might cause considerable degradation in solid-propellant motors. The degrading effects of vacuum and radiation on solid propellants may be predicted from theory in only a very limited manner. Thus, one may predict, for example, volatility, diffusion rates, and susceptibility to radiation of some specific propellant components or combinations of components. But, to predict reliably how these variables interact in a propellant stored in space is not possible. It follows, then, that one must devise certain experimental means to predict the storage reliability of propellants in space. A simple space-storage test, however, cannot be made either, because of the difficulty in duplicating space conditions. It has been necessary, therefore, to call upon theory as an aid in designing and interpreting the experiments, which might otherwise have been considered routine tests.

In 1963, a space-storage study was completed by Battelle^{(1)*}. Its purpose was to evaluate certain solid propellants with regard to their stability during space storage. Two "basic" composite propellants were examined, one based on a PBAA binder, the other on a polyurethane binder. Compositions were chosen to be as simple as possible; that is, in addition to NH_4ClO_4 , Al powder, and binder, only the additives necessary for polymerization were used. These propellants were exposed to cobalt-60 radiation or to extended periods of vacuum storage, and propellant specimens were then tested for rheological and combustion properties, i. e., tensile strength, secant modulus, per cent strain at maximum load, shore hardness, swelling, weight loss, autoignition temperature, ignition time, and burning rate.

Briefly summarized, the results of the study indicated that prolonged vacuum exposure produced some relatively small changes in mechanical properties. There was good evidence that, in the PBAA propellant, the increase in tensile strength, secant modulus, and shore hardness were brought about by the removal of a small quantity of a material that acts as a plasticizer, although no plasticizer was intentionally included. Burning properties were not appreciably affected by prolonged vacuum exposure. Gamma irradiation resulted in greater changes in rheological and burning properties, but only at doses corresponding to several years in the Van Allen belt.

The results of the research were valuable in that they gave a general picture of the effects to be expected in "basic" propellants. They were incomplete in that actual working propellants were not investigated. Specifically, the behavior of the many additives commonly incorporated in practical propellant formulations was purposely excluded from the study. Many plasticizers, burning-rate modifiers, antioxidants, etc., are relatively volatile materials and could be lost by evaporation.

The purpose of the present study differs from that of the previous one in that the current program was not to consider the effects of space environment on solid propellants but was to investigate the rate of loss of certain representative additives during vacuum exposure.

*References are listed at the end of the report.

Two properties of an additive in combination with a solid propellant can influence the rate of loss of the additive in vacuum. The first is its vapor pressure. Plainly, materials of very low vapor pressure will not be lost by evaporation. The polymer itself will be unaffected. Some NH_4ClO_4 may evaporate, but the amount lost and the effect will be negligible. Materials such as copper chromite, iron oxide, and carbon will not vaporize at ordinary temperatures. On the other hand, materials having vapor pressures of the order of 10^{-6} torr, which would ordinarily be considered involatile, may undergo appreciable loss in the vacuum of space.

If the vapor pressure of the additive, in solution or dispersed in the binder, is known, then the rate of loss from the surface can be calculated. The rate at which the material moves through the solid phase to the surface will be the limiting rate for all materials of appreciable vapor pressure. The second important property to be investigated, therefore, is the diffusion coefficient, which is a measure of the rate of diffusion through the polymer matrix. Thus, materials with high vapor pressures will not necessarily be lost more rapidly than those with low vapor pressures. Although it may be anticipated that smaller molecules will have both higher vapor pressures and higher diffusion coefficients, this loss can be demonstrated only by experiment.

The present program was undertaken with the intention of investigating a number of additives in one or two binder systems. A review of additives currently in use in solid-propellant applications was carried out. Three additives were chosen as representative for this program; these were all volatile materials relative to space-storage environment. The additives selected for study were ferrocene (burning-rate modifier), dioctyl adipate (plasticizer), and phenyl-beta-naphthylamine (antioxidant). The last of these received the least attention in this program because, during the course of the work, it became necessary and feasible to modify the apparatus and procedures to provide accurate temperature measurement simultaneously with the weight-loss measurement. The work was also expanded to include concentration of the additive as a variable. As a result, the number of additives studied in detail was reduced to two. As will be seen, these additives covered a wide span of vaporization rates but differed only slightly in diffusion rates.

Experimentally, one obtains the vapor-pressure data and diffusion data in the same manner, that is, by following the weight loss of material as a function of time. This is carried out for the pure additive or the propellant-additive combination, as the case may be. Because of the nature of the experiments, vapor pressure and diffusion data were not obtained in any special sequence in the program. For ease of examination, however, the results of the vapor pressure and diffusion studies are discussed separately in the next sections.

VAPOR-PRESSURE STUDIES

The vapor pressures of the three additives considered in this program have been studied. This has been done to obtain background information on the additives and on the method, and also to prepare for a study of the effective vapor pressures of propellants containing the additives. It should not be supposed that the higher the vapor pressure the more readily will a component be removed from the propellant. Both vapor pressure and rate of diffusion are significant in this regard.

Vaporization Theory

The kinetic theory of gases yields the following equation for the loss of material from a pure substance into a perfect vacuum:

$$G = 5.82 \times 10^{-2} \alpha A t p (M/T)^{1/2} \quad , \quad (1)$$

where

G = weight loss in grams

α = condensation coefficient

A = vaporization area in cm^2

t = time in sec

p = vapor pressure in torr

M = molecular weight

T = absolute temperature in degrees K.

In the development of the equation, the equilibrium between the condensed phase and its vapor is considered. The condensation coefficient, α , is defined as that fraction of the molecules striking the surface that condense. It has been found that, for most cases of simple vaporization, this coefficient is equal to unity, and the assumption has been made that such is the case here.

Two methods have been used, commonly designated as the Langmuir vaporization and the Knudsen effusion methods. In the first, the surface of the sample is exposed directly to the vacuum in such a way that the vaporizing molecules cannot return to the surface. The area, A , is then the total exposed surface area. Experimentally, one measures G , the weight loss, over a period of time, and the vapor pressure is obtained by substituting in Equation (1).

In the Knudsen effusion method, the sample is placed inside a cell that is provided with an orifice of known area. The surface of the sample is sufficiently large to maintain a saturated atmosphere inside the cell. Thus, the vapor phase is studied directly in this method and the condensation coefficient, α , does not enter in Equation (1). The area, A , is the area of the orifice; all other terms have the same significance as before. The dimension of the orifice must be small in comparison with the mean free path of the molecules. That is to say, the molecules must not stream out by colliding with one another, but must individually find their way through chance collision with the walls.

Experimental

Apparatus

Experiments were conducted by a technique involving the continuous weighing in vacuum of a specimen while evaporation took place in a controlled manner. A sketch and photograph of the sample environment are shown in Figures 1 and 2. The sample was suspended in vacuum from a microbalance. It was surrounded by a "cage" heater, which maintained it at the desired temperature while interposing very little obstruction in the way of vaporizing molecules. Vaporized material passed through the heater to the wall of the apparatus and there was condensed at liquid-nitrogen temperature. A vacuum of about 10^{-6} torr was maintained. For a pure material the rate of weight loss, G/t , is constant. The vapor pressure is found from Equation (1).

A Sartorius model Electrona I torsion balance was used. A rough balance was obtained before closing the vacuum system by adjusting counterweights. A further adjustment could be made by imparting a twist to the calibrated torsion-wire suspension. Final balance was obtained automatically by electronic adjustment of a magnetic field. This final adjustment was recorded on an 11-inch chart, for which full scale corresponded to 1 mg. Weight changes were recorded with a sensitivity of $1\text{ }\mu\text{g}$, except that sometimes instability limited the sensitivity to about $10\text{ }\mu\text{g}$. The range available without breaking the vacuum was 6 mg, including the torsion-wire adjustment.

It became apparent early in the program that a direct, simultaneous reading of sample temperature and sample weight would be necessary to accomplish the goals of this work. Taking advantage of the fact that the balance is a null instrument, project personnel devised a modification that worked well. The sample was supported from the balance arm by means of a 3-mil Chromel-Alumel thermocouple. The connection between this couple and the fixed leads passing through vacuum seals was made with short lengths of 1/2-mil Chromel and Alumel wire. These fine wires introduced no intolerable disturbance into the balance system. As indicated, the use of such a suspension was possible only because the balance is a null instrument so that, at balance, the sample and suspension were always at the same position. The temperature of this thermocouple, which was embedded in the sample, was recorded continuously.

The Sartorius balance was chosen for use in this program because of its high sensitivity. The course of the work was plagued, however, by an intermittent instability in the electrical control circuit of the balance. The effect, while extremely troublesome, was usually small compared to the magnitude of the weight changes observed, so that it is presumed to have introduced no appreciable uncertainty into the results. On the other hand, the balance was remarkably stable toward vibrations in support structure. It was therefore not necessary to provide any special vibration damping.

The heater, shown in Figure 1, was made of 5-mil platinum wire supported at the top and bottom on quartz rings. The upper ring was supported by wires (not shown in the figure) from the wall of the apparatus. A weight hanging from the lower ring kept the wires fairly taut. Current was supplied through copper leads (omitted from Figure 1); the heater was placed in series with a rheostat and supplied with about 12 volts. A temperature controller operated a switch across the rheostat, thus giving a high-low control. The sensing element for this temperature control was a thermocouple positioned just below the sample, as shown (without the leads) in Figure 1.

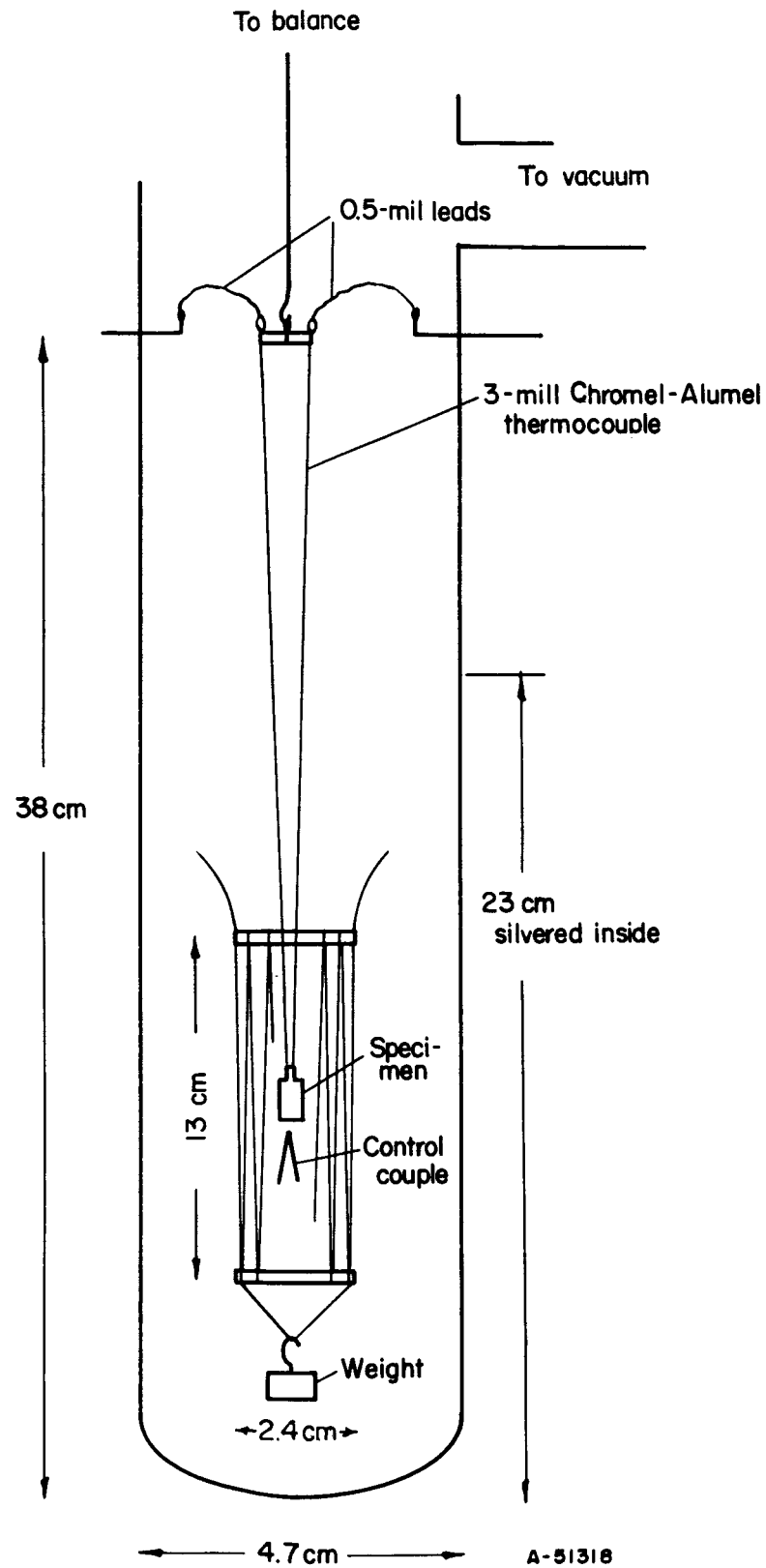
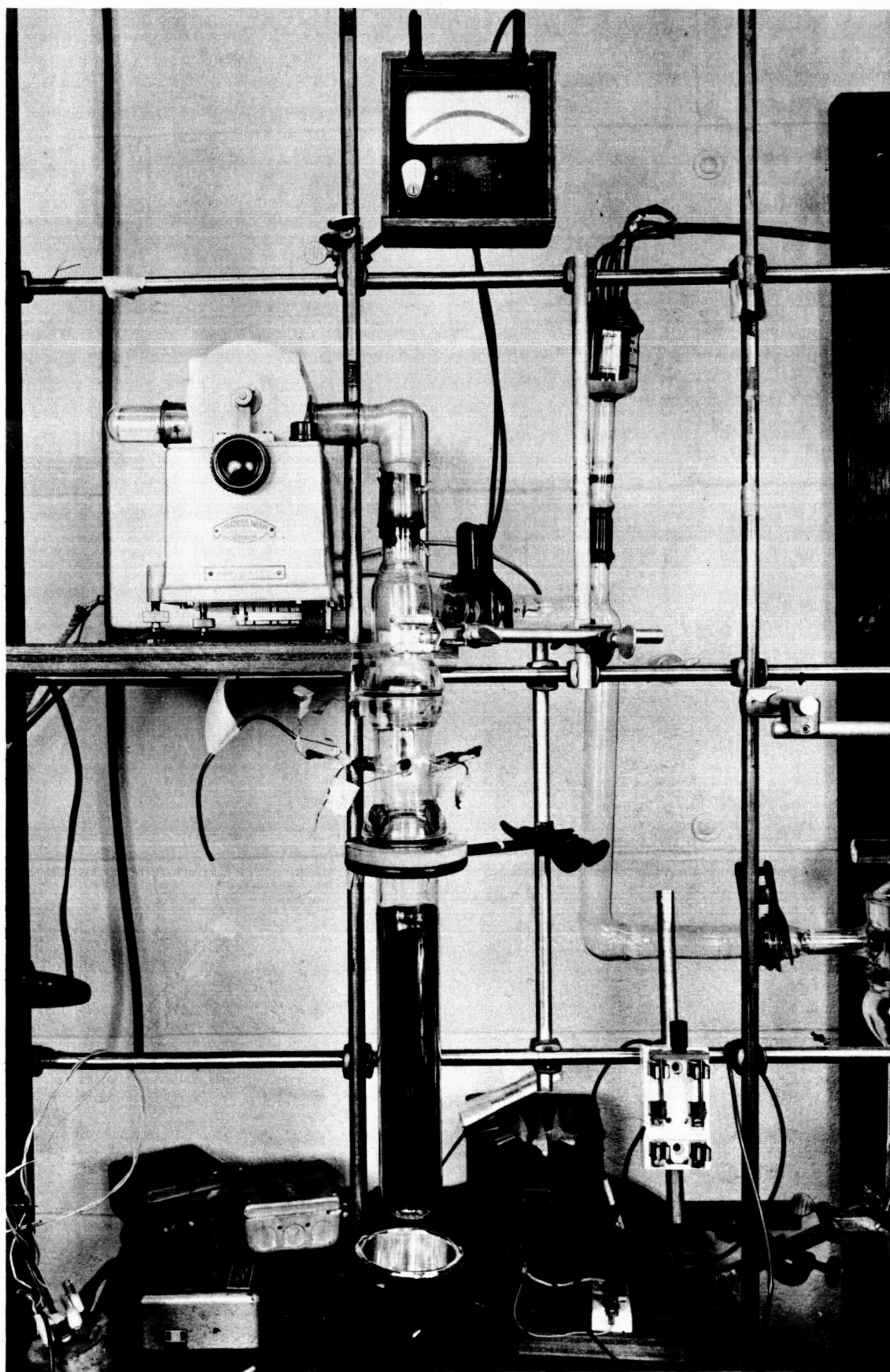


FIGURE 1. APPARATUS FOR VAPORIZATION AND DIFFUSION STUDIES



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FIGURE 2. MICROBALANCE AND ASSOCIATED APPARATUS
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This simple control system gave temperature fluctuations in the sample couple with a period of about 1 minute and an amplitude of about 1°C. The heater was adequate, provided a vacuum was maintained and the inside of the cold wall was silvered.

In order to maintain constant temperature within the sample, it was necessary that the level of liquid nitrogen remain constant to within 1/2 inch or less. This was accomplished by means of a simple level control. Two thermistors were used as sensors, one being positioned about 1/2 inch above the other, taped to the outside of the tube at about the upper limit of the silvered portion. When both thermistors were above the liquid level, current was passed through them to open a solenoid valve. The valve admitted nitrogen gas to a Dewar of liquid nitrogen, forcing the liquid into the container that surrounded the apparatus. When the level rose to cover both thermistors, the valve closed and the flow stopped. The frequency of transfer and the sensitivity of level control were governed by the vertical distance between the thermistors. This device proved reliable, allowing the experiment to proceed unattended. These components are omitted from Figure 2, as were the recorders and the temperature controller.

Procedure

The Langmuir vaporization studies were used to measure small vapor pressures, since the effective vaporization area is equal to the total surface area of the specimen. The ferrocene and phenyl-beta-naphthylamine specimens were prepared by dipping a cylinder of porcelain or graphite, approximately 1/4 inch in diameter and 1/2 inch long, into the molten sample, thus forming a thin coating on the mandrel. An axial hole was drilled through half the length to accommodate the thermocouple tube, and the exposed area was determined from dimensional measurements. Attempts to use such a dipping procedure for dioctyl adipate, which is liquid at room temperature, proved unsuccessful. A cast sample of ferrocene, about the same size, was also used.

The Knudsen effusion studies were carried out in a cell fabricated from brass and soft solder. The cell contained a re-entrant thermocouple well and was supported by the thermocouple in the same manner as in other experiments. The 1/16-inch effusion hole was located on the side, so that the vapor stream was directed toward the cold wall. A small amount of a silicone polymer was painted on the area around the effusion hole to prevent the liquid from creeping out. Knudsen determinations were made on all three additives.

Results

Dioctyl Adipate. Two samples of dioctyl adipate were used. The first was a commercial plasticizer grade. The second was a sample of bis(2-ethyl-hexyl) adipate, obtained from Matheson, Coleman, and Bell. Some Langmuir experiments were attempted with a graphite cylinder soaked in the first material. The results appeared to indicate a continuously falling vapor pressure, which may have been due to the loss of low-boiling components from the sample. Knudsen effusion measurements were made with more-nearly-pure material. The results are shown in Figure 3. The first few points (not shown) lie above the line, indicating the presence of a small amount of more volatile impurity. The data fit the relationship

$$\log p \text{ (torr)} = 11.90 - 5397/T$$

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(2)

This is in good agreement with the stated boiling point of the sample (207-208°C at 4 torr).

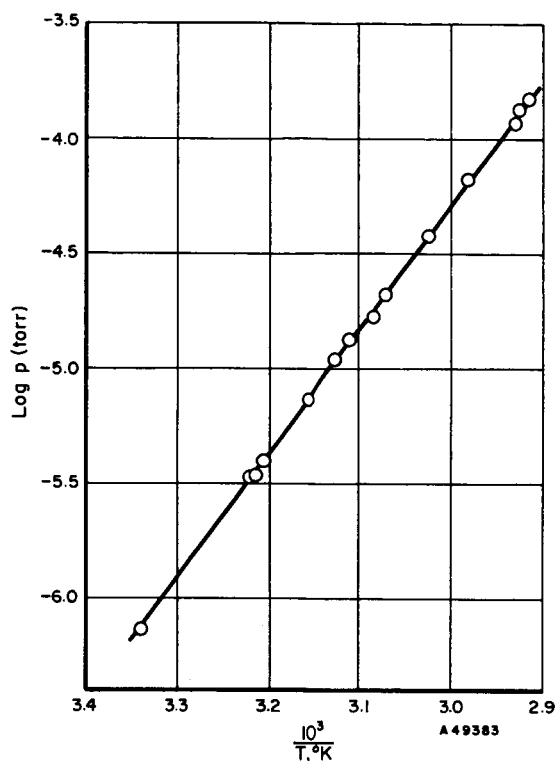


FIGURE 3. VAPOR PRESSURE OF BIS(2-ETHYL-HEXYL) ADIPATE

Ferrocene. Langmuir vaporization studies were carried out on two samples of ferrocene. The first material was obtained from Du Pont. It was cast in a steel mold, using a small amount of Fiberglas as reinforcement. The sample was 1/4 in. in diameter and 1/2 in. long. The second sample was prepared from material obtained from Peninsular ChemResearch, Inc. of Gainesville, Florida. The sample was twice sublimed before use. A cylindrical piece of porcelain was dipped into the molten sample to form the second specimen.

The vapor-pressure results are shown in Figure 4. Three points determined by effusion experiments in a previous program⁽¹⁾ are also shown, as is an extrapolation of the line obtained by Edwards and Kington⁽²⁾. The new data fit the line

$$\log p \text{ (torr)} = 10.96 - 3947/T \quad . \quad (3)$$

The agreement with older data is satisfactory.

Phenyl-beta-naphthylamine. The sample used in this work was obtained from the U. S. Bureau of Standards (Standard Sample No. 377). A cylindrical specimen was prepared for Langmuir measurements by dipping a piece of graphite into the molten sample. Knudsen effusion measurements were also made.

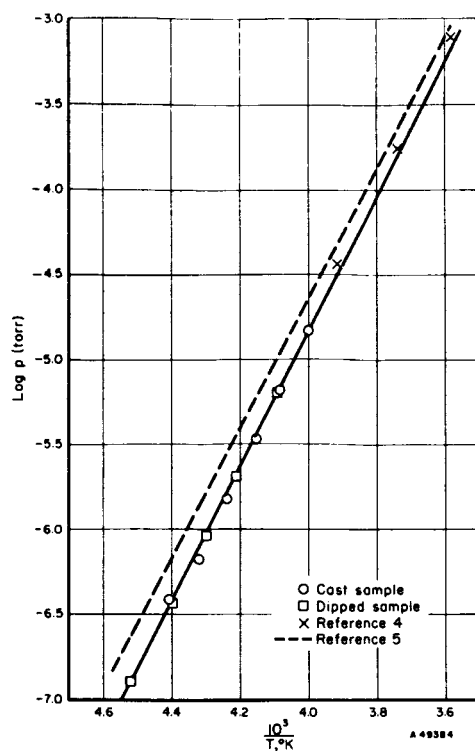


FIGURE 4. VAPOR PRESSURE OF FERROCENE

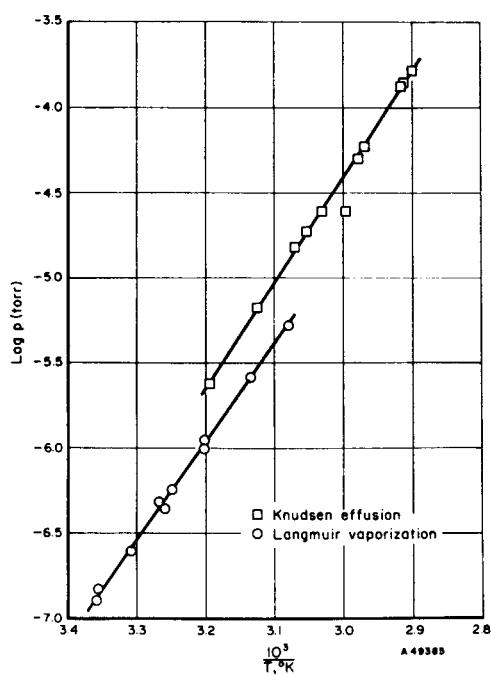


FIGURE 5. VAPOR PRESSURE OF PHENYL-BETA-NAPHTHYL AMINE

Vapor-pressure results are shown in Figure 5. The results did not seem to be very satisfactory, in that there appeared to be a drift toward lower values in some cases. This drift occurred in both the Langmuir and the Knudsen experiments. Plainly, the two methods do not agree very well. The Knudsen effusion results are to be preferred, but confidence in these results is somewhat less than for the other two materials studied. The presentation of an analytical expression for these data does not seem to be justified.

DIFFUSION STUDIES

In the preceding section, the rate of weight loss of a pure material was used as a method of determining the vapor pressure. The same method was used with propellant specimens to determine the diffusion constant of additives. The fact that diffusion experiments were carried out in vacuum and that additives are lost from propellants in rockets exposed to the vacuum of space is only coincidental. Diffusion coefficients could have been determined by some method not involving the use of vacuum. As will be shown later, the results do not serve directly as a measure of the loss of additives from a rocket in space.

The Diffusion Law

The well-known "Second Law of Diffusion" in one dimension can be written

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) , \quad (4)$$

where C is the concentration of the diffusing species, x is the distance, t is the time, and D is the diffusion coefficient. If D is a function of concentration, the equation is difficult to apply to experimental data. The equation has been solved for many specific cases in which D is constant. By comparing experimental results with these standard solutions, one can obtain an approximate value of the diffusion coefficient and thus obtain some idea of its constancy. For cases of simple diffusion, D can be found precisely.

The method is to start with a specimen of uniform concentration of additive, C_1 , and then to reduce the concentration at the surface to near zero by evaporation in a vacuum. A cylindrical sample is convenient experimentally, although somewhat awkward analytically. In a cylinder of radius a , where the conditions are

$$C = C_1, \quad 0 < r < a, \quad t = 0 ,$$

$$C = 0, \quad r = a, \quad t > 0 ,$$

the quantity of diffusing substance, M_t , that has left the cylinder in time, t , is given by

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} e^{-D \alpha_n^2 t} \quad (5)$$

M_∞ is the quantity leaving the cylinder at infinite time. The n 's are the positive roots of

$$J_0(a \alpha_n) = 0 \quad , \quad (6)$$

where $J_0(x)$ is the Bessel function of the first kind of order zero. A plot of Equation (5) in terms of $(Dt/a^2)^{1/2}$ is available.⁽³⁾ For small times the equation

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{a^2} \right)^{1/2} - \frac{Dt}{a^2} - \frac{1}{3\pi^{1/2}} \left(\frac{Dt}{a^2} \right)^{3/2} \quad (7)$$

may be used. For very small times, only the first term is significant. If D is a function of concentration, these relationships will yield a value of D corresponding to some concentration between C_1 and 0. Several diffusion runs on cylindrical samples have been treated with the aid of these equations; these analyses are shown in a later section of this report.

For a plane sheet of thickness 2ℓ , applying similar conditions, the quantity of diffusing substance is given by

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-\frac{(2n+1)^2 \pi^2 Dt}{4\ell^2}} \quad (8)$$

For small times, the equation

$$\frac{M_t}{M_\infty} = 2 \left(\frac{Dt}{\ell^2} \right)^{1/2} \left[\frac{1}{\pi^{1/2}} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} \frac{n\ell}{(Dt)^{1/2}} \right] \quad (9)$$

may be used. The function $\operatorname{ierfc}(x)$ is also available in tables.⁽³⁾ Equation (9) shows that for small times, the loss is proportional to $t^{1/2}$, as in the cylindrical case according to Equation (7). The diffusion coefficient can be determined from the initial linear portion of the plot of M_t/M_∞ versus $t^{1/2}$.

The condition $C = 0$ at the surface, for which the equations were derived, cannot be satisfied exactly. The concentration at the surface is made as low as possible experimentally by trapping all the material vaporized; under this condition, none of the diffusing and vaporizing material can return to the surface of the specimen. Shortly after the beginning of an experiment, the surface concentration will have been reduced sufficiently to allow the application of these equations.

Sample Preparation

Since the vaporization of specific additives from solid propellants was to be studied, it was necessary to prepare small quantities of propellant samples containing minimum amounts of volatile constituent. Extraneous wetting agents, plasticizers, etc., were therefore omitted from the basic formulation. Some development work was carried out to establish the procedure for producing sound specimens of almost zero volatility.

Only polyurethane specimens were examined in the program, but a limited amount of development work was also initiated with PBAA formulations.

The compositions of the polyurethane fuels used are shown in Table 1. The ammonium perchlorate was a standard Air Force blend furnished by Aerojet-General Corporation. The aluminum powder was a standard fuel grade obtained from Reynolds Metals Company. The dioctyl adipate (DOA) was commercial plasticizer grade. The phenyl-beta-naphthylamine (PBNA) and ferrocene were used without purification.

TABLE 1. COMPOSITION, CONDITIONS FOR PREPARATION,
AND HARDNESS OF POLYURETHANE FUELS

Sample Number:	Weight Per Cent				
	30-1	30-2	43-1	46-1	51-1
Ammonium Perchlorate	65.5	65.5	65.5	65.5	65.5
Aluminum Powder	8.0	8.0	8.0	8.0	8.0
Binder(a)	26.5	26.5	26.5	26.5	26.5
DOA	--	3.0(b)	--	--	--
PBNA	--	--	0.25(b)	--	--
Ferrocene	--	--	--	1.0(b)	--
Time Additive Under Vacuum, minutes	--	10	15	15	--
Cure Cycle, hr/°F	16/130+	16/130+	16/130+	16/130+	16/130+
	16/180	16/180	16/180	3/200	3/200
Hardness, Shore A2	95	89	95	93	94

(a) Toluene diisocyanate-polyurethane.

(b) Per cent of total weight of charge.

Samples 30-1 and 30-2 were mixed in a Model 60LP Vertical Mixer manufactured by the Atlantic Research Corporation. The other samples were prepared in a Model 2 CV Mixer, also from Atlantic Research Corporation. The binder was introduced first into the mixer and degassed under vacuum for approximately 1/2 hour. The aluminum powder and predried oxidizer were then added, and mixing was continued for 1 hour under vacuum with cooling water on the mixer jacket. The additives were incorporated during the last 10 to 15 minutes of the mixing cycle in order to reduce their time under vacuum.

At the end of the mixing cycle, Samples 30-1 and 30-2 were dumped into an open container, preheated to approximately 110°F, and then cast into molds made from polyethylene bottles. These molds were then placed in a vacuum oven, heated to approximately 110°F, and subjected to vacuum for about 5 minutes. The molds were returned to ambient pressure and vibrated for about 5 minutes. These steps were repeated until the material appeared to be free of air bubbles. The samples were then cured for 16 hours at 130°F, followed by 16 hours at 180°F. The molds were stored in a desiccator over Drierite until used.

The remaining samples, mixed in the Model 2 CV Mixer, were extruded directly from the mixer into polyethylene molds. Degassing and vibration were carried out as with the previously described samples. The samples were cured for 16 hours at 130°F, followed by either 16 hours at 180°F or 3 hours at 200°F. On the basis of hardness results, the shorter cycle at a higher end temperature produced specimens equivalent to those obtained with the longer cure cycle. These samples were also stored in desiccators.

Diffusion in Cylindrical Samples

Procedure

Cylindrical propellant specimens were cut to standard dimensions, 6 mm in diameter and 13 mm long, and weighed about 0.6 g. Specimens were prepared from each of the materials shown in Table 1. Aluminum-foil disks were cemented to the ends of these cylinders to restrict diffusion to the one radial direction. A 1.5-mm thermocouple hole was drilled axially to the center of each specimen. During the experiment, the specimen was supported by a thermocouple tube that fit into this hole. Desorption experiments were carried out with specimens cut from each sample of Table 1. The procedure in these experiments was essentially the same as that used in the vapor-pressure determinations. It can be seen from the theory that the rate of weight loss, which is constant for vapor-pressure determination, is not constant for diffusion experiments. As shown in Equation (7), the weight loss is a linear function of $t^{1/2}$ in the initial part of the experiment. Since all samples contained some volatile material, it was necessary to subtract the weight loss of a "blank" sample from the weight loss of the sample containing additive. The net weight loss was then plotted against $t^{1/2}$, and the diffusion constant was found by comparison with curves calculated from Equations (5) and (7).

Results

Diocetyl Adipate. The fractional weight loss of Sample 30-2 less the weight loss of "blank" Sample 30-1 was determined and plotted as a function of $t^{1/2}$. The results are shown in Figures 6 and 7. The curve of Equation (5) and (7) is shown for comparison, based on the indicated values of D . The data obtained at 68.6°C follow the theoretical curve well, but the results at 29.0°C are inconclusive. This latter experiment continued for about 2 days, at which point only about 18 per cent of the diocetyl adipate had vaporized. It seems likely that the blank sample was not truly comparable with the sample containing the additive.

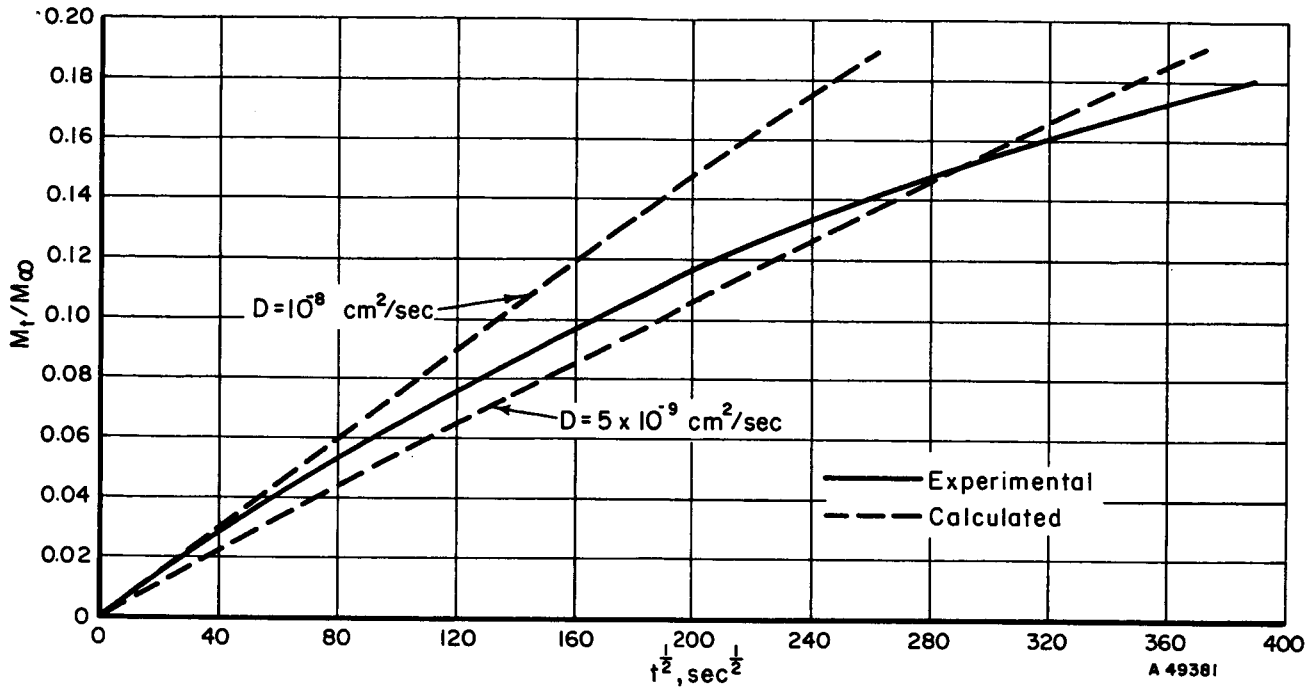


FIGURE 6. DIFFUSION OF DIOCTYL ADIPATE IN POLYURETHANE PROPELLANT AT 29.0°C

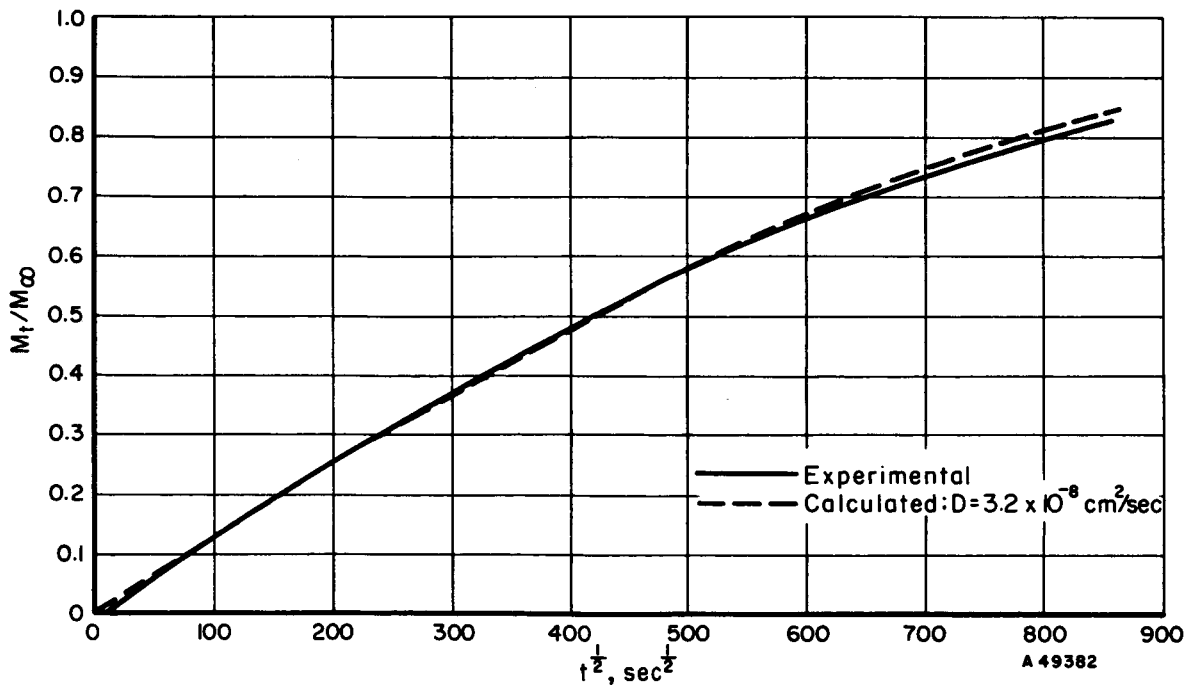


FIGURE 7. DIFFUSION OF DIOCTYL ADIPATE IN POLYURETHANE PROPELLANT AT 68.6°C

Ferrocene. Weight-loss measurements were made with Sample 46-1, containing 1 per cent ferrocene, at only one temperature. The results, after subtracting Blank 51-1, are shown in Figure 8. After the first hour, a reasonably straight line was obtained for about 16 hours. Equation (7) gives, from this linear portion, $D = 3.64 \times 10^{-8}$ cm²/sec at 68.6°C. The calculated curve for this diffusion coefficient is also shown in Figure 8. The two curves are displaced because of the initial curved portion of the experimental curve. This is probably due to a difference in the binder of the two propellant formulations.

Phenyl-beta-naphthylamine. A single desorption experiment with phenyl-beta-naphthylamine at 68.4°C yielded unsatisfactory results. During the first portion of the run, the weight loss was less than in the case of the corresponding blank determination. The samples were plainly not comparable. Since only 1/4 per cent of additive was used, only about half the total loss was due to the additive. The failure in obtaining equivalent propellant samples was more serious than for the other additives. A somewhat arbitrary procedure for correcting the results was used, leading to a diffusion coefficient between 1.5×10^{-8} and 3×10^{-8} cm²/sec. The diffusion rate therefore appears to be similar to that observed for the other two additives.

Diffusion in Flat Samples

Procedure

Because of the excessive time required for each determination with the cylindrical samples, additional determinations were made with thin flat specimens. To avoid the uncertainties involved in comparing each sample with a blank, a revised method of incorporating the additive was adopted.

Slab specimens were cut from propellant Sample 51-1, which contained no additive but did contain about 1/4 per cent volatile materials. The specimens, each weighing about 150 mg, were 1 cm square and 1 mm thick. A small incision, about 3 mm deep, was cut into one edge of each for the insertion of the thermocouple bead.

The samples were hung in the upper part of a vertical 2-inch tube provided with a vacuum pump. The lower part of the tube was immersed in liquid nitrogen; the upper part was wrapped with a heater. For several days, the samples were kept at about 100°C in a good vacuum and close to a cold surface where volatiles could condense. The weight loss was about 1.2 per cent, representing, in addition to the easily volatile material, a part of the NH₄ClO₄. The surface loss of oxidizer is about 1 per cent of the total amount of oxidizer. One of these specimens and one that did not receive this vigorous degassing were used for a series of sorption-desorption experiments, as will be described shortly.

The plasticizer dioctyl adipate was introduced into the specimens by a method of prolonged sorption. Inside each of several weighing bottles, three specimens were hung from a wire framework. A known quantity of pure plasticizer [bis(2 ethylhexyl) adipate, boiling point 207-208°C at 4 torr] was placed into the bottom of each bottle. The closed bottles were kept at about 100°C for 4 days. One of the bottles contained plasticizer equivalent to 3.3 per cent of the propellant sample weight. After 4 days at 100°C, some liquid was still visible on the glass walls. This bottle was heated for an

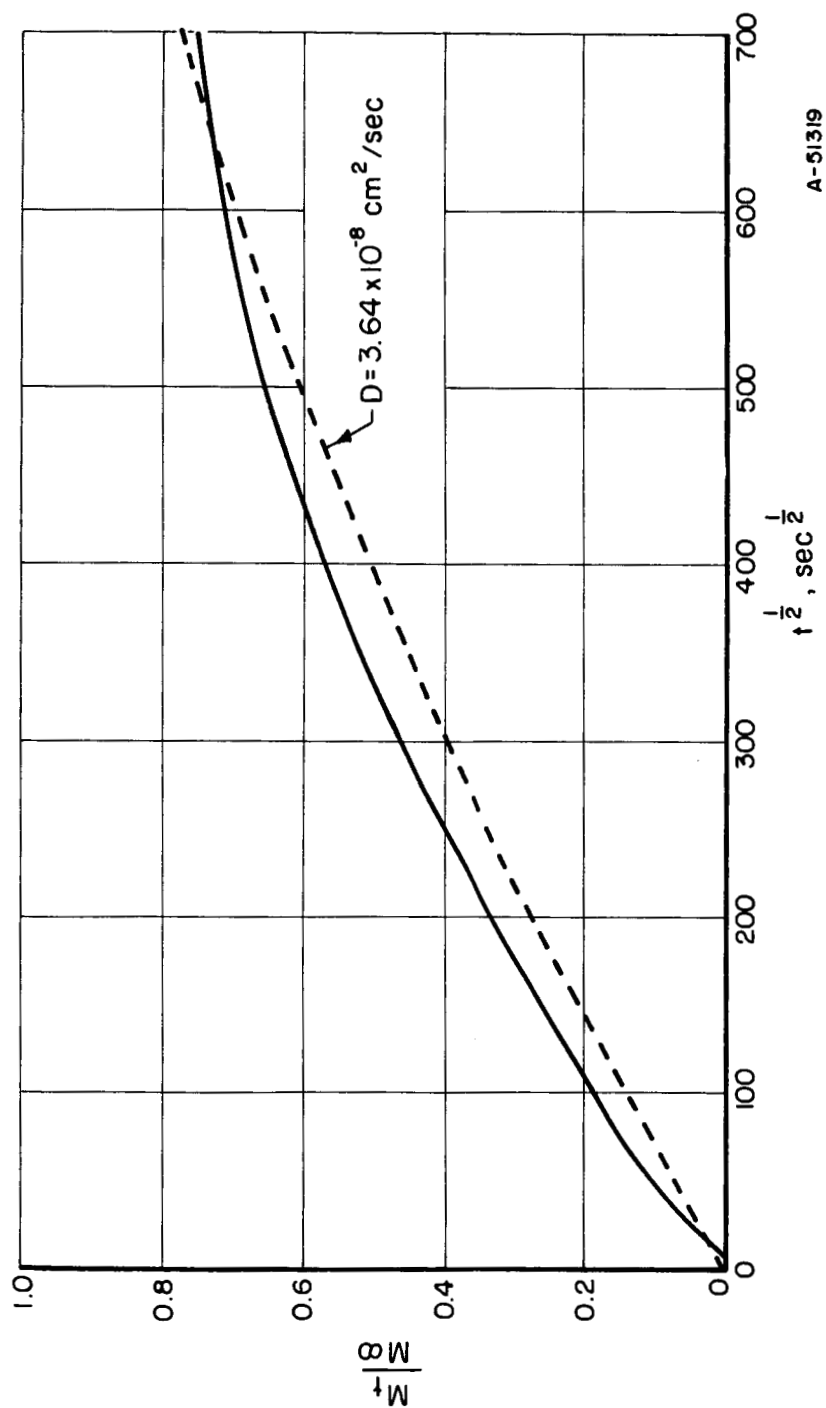


FIGURE 8. DIFFUSION OF FERROCENE IN POLYURETHANE PROPELLANT AT 68.6°C

additional period of 5 days, after which liquid was still visible. Later analysis showed that the samples had sorbed plasticizer equal to 2.8 per cent of their weight. This is presumed to be the equilibrium concentration at 100°C. The other bottles contained less plasticizer, all of which was absorbed by the propellant samples.

Desorption experiments were carried out with specimens prepared in this way, the procedure being approximately the same as for the cylindrical specimens previously described. The specimens were suspended from the balance arm by means of the thermocouple, the bead being inserted into the slot cut into the edge of the specimen. The experiment was begun by pouring liquid nitrogen around the tube while raising the temperature of the specimen to the level chosen for the experiment. After weight changes were recorded for a day or more, the temperature was raised to 70°C to complete the desorption, so that the total amount of additive could be determined.

Two specimens, as previously noted, were subjected to a prolonged series of sorption-desorption experiments. With a thoroughly degassed specimen hanging from the balance arm, with dioctyl adipate on the walls of the tube, and the tube remaining at room temperature, and with the pressure reduced to about 10^{-4} torr, the space inside the apparatus was saturated with respect to dioctyl adipate at a vapor pressure of about 10^{-6} torr (the equilibrium vapor pressure at room temperature). The plasticizer was absorbed by the specimen at a rate that depended on the rate of diffusion into the propellant. The same equations apply as for desorption. If Fick's law of diffusion [Equation (4)] is followed, and if D is not dependent on concentration, then the rate of sorption will be the same as the rate of desorption at corresponding times and temperatures.

Several degassed propellant specimens were loaded with ferrocene in a modification of the procedure used with dioctyl adipate. The specimens were hung inside a glass tube, which also contained a known amount of ferrocene. The tube was evacuated and sealed, while being kept cold to prevent loss of the ferrocene. From later experiments, it became apparent that some water was inadvertently introduced at this point. The tube was then kept at 100°C for 3 days to allow sorption and equilibration of the ferrocene. These specimens contained about 1 per cent ferrocene. Diffusion experiments by desorption were carried out in the same manner as those with the dioctyl adipate specimens. Several sorption-desorption runs were also conducted after traces of dioctyl adipate and pump oil were carefully removed from the walls of the apparatus.

Results

Dioctyl Adipate. Six specimens, prepared by sorption of pure dioctyl adipate at 100°C into previously outgassed propellant specimens, were desorbed at three temperatures. The results, in terms of fractional weight loss plotted versus $t^{1/2}$, are shown in Figures 9 and 10. In each figure, the dashed straight line shown is a calculated line obtained by fitting a diffusion coefficient into Equation (9). In all cases but one, the data follow the line well. The data of Figure 9a and Figure 10a fit fairly well the calculated curve (not shown) beyond the straight-line portion.

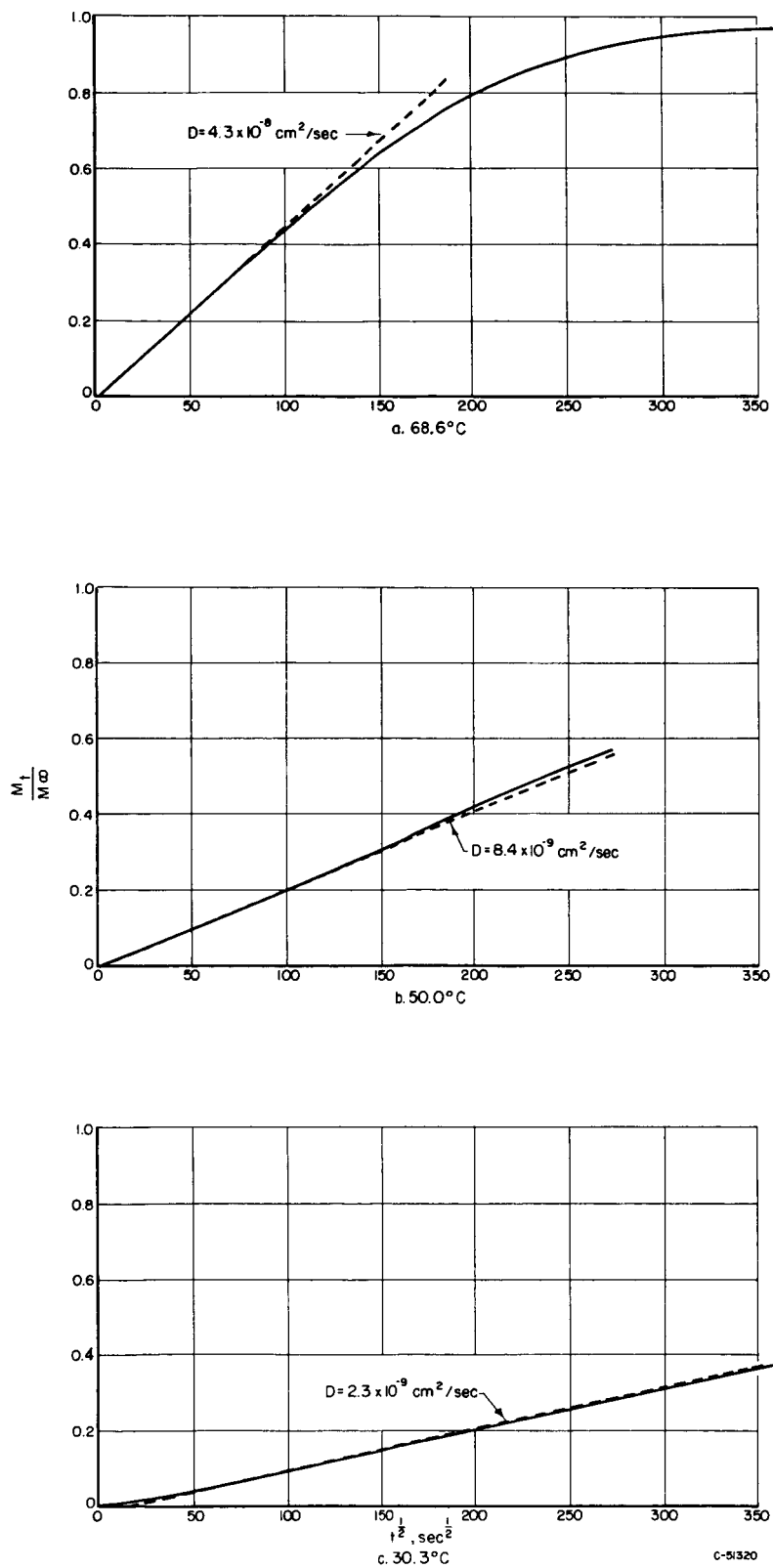


FIGURE 9. DIFFUSION OF 2.8 PER CENT DIOCTYL ADIPATE FROM FLAT SLAB AT 68.6, 50.0 AND 30.3°C

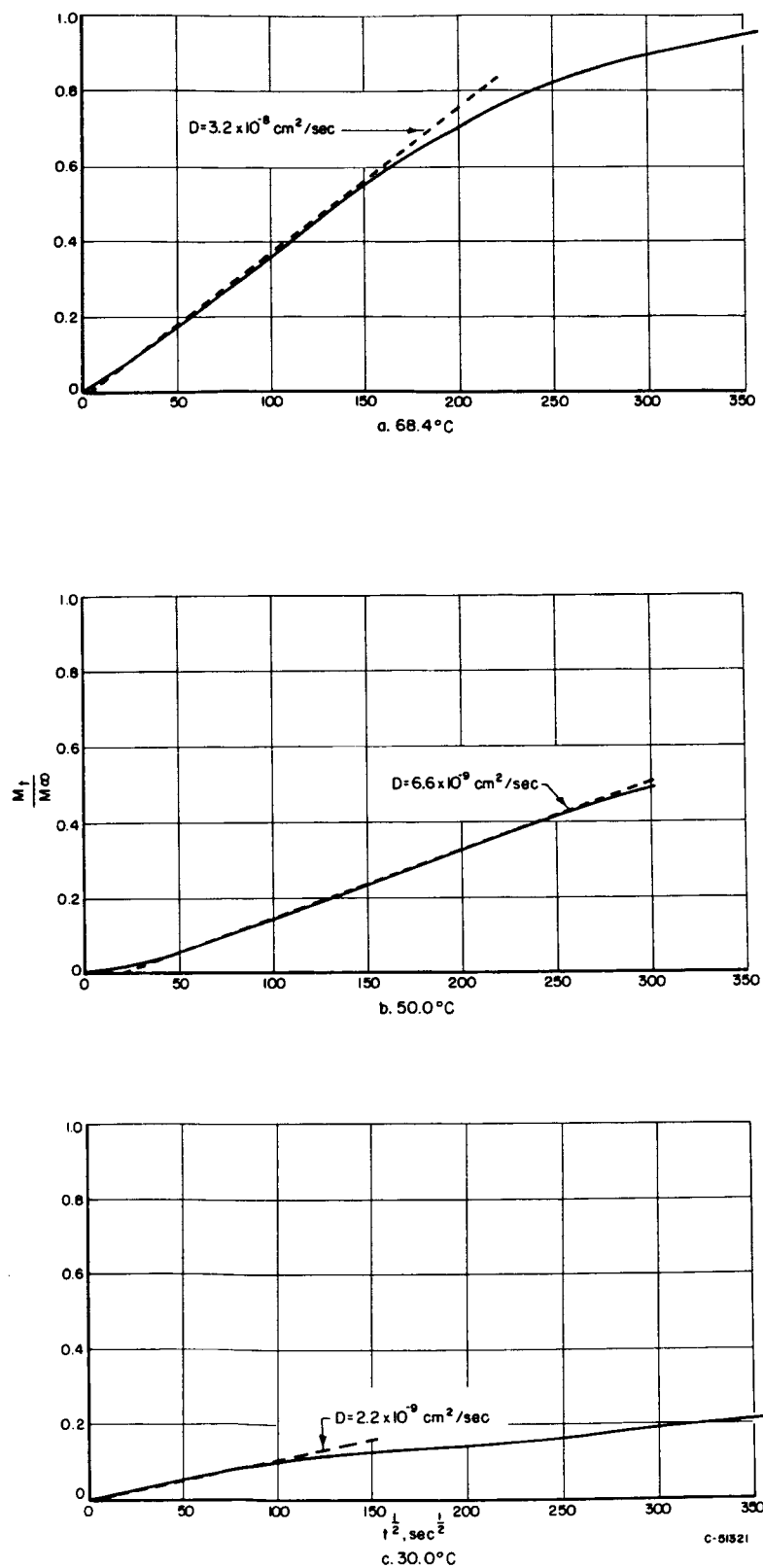


FIGURE 10. DIFFUSION OF 1.2 PER CENT DIOCTYL ADIPATE FROM FLAT SLAB AT 68.4, 50.0 AND 30.0°C

In most cases the straight-line portion of the curve does not pass through the origin. The reason for this is that in the early part of the run the weight loss is not diffusion controlled but is limited by the rate of vaporization from the surface. The data in Figures 9b, 10a, and 10c deviate somewhat from the straight line for unknown reasons. In the case of Figure 10c, this deviation is so marked as to cast serious doubt on the result. With the exception of this, the results appear to be satisfactory.

The sorption-desorption experiments were intended to be exploratory. They produced some interesting and puzzling results, but the data were not as reliable as those previously reported. A few examples of the weight-change curves found in these experiments are shown in Figures 11 through 13. A freshly cut specimen was hung from the microbalance and desorbed at about 68°C for 36 hours. The tube was then cleaned, and a small amount of dioctyl adipate was introduced into the bottom. After evacuation, the sample was maintained at 49.9°C, the tube remaining at room temperature, until sorption appeared to be complete. The weight change for the first part of the run is shown as a function of $t^{1/2}$ in Figure 11. The plot shows M_t rather than M_t/M_∞ , because the total amount sorbed is uncertain. The data are not suitably linear because of balance instability at these low magnitudes of weight change. When, after about 2 days, the weight appeared to be constant, a desorption run was made, the walls being cooled with liquid nitrogen. The results for 4 hours are shown in Figure 12. The data fit a straight line fairly well. The desorption was completed at 68°C in another 21 hours. A second sorption was undertaken by removing the liquid nitrogen and warming the tube to room temperature. The results are shown in Figure 13. The latter part of the run shows the effect of variable room temperature on the vapor pressure of the dioctyl adipate. The first part follows the straight line well. If one assumes a total of 0.12 mg at saturation, the calculated diffusion coefficients are, in order, 1.8×10^{-8} , 1.9×10^{-8} , and 9.3×10^{-8} cm²/sec, all at approximately 50°C.

In the experiment just described, there is some uncertainty due to balance instability; also there is some doubt in the value of M_∞ because of variable room temperature. These difficulties might introduce as much as 20 or 30 per cent uncertainty into the calculation of the diffusion coefficient. The high value of the third determination cannot be explained so readily. The rate of weight change was so much greater than in the previous two cases that it must be the result of some major change in the specimen or experimental conditions. The reason for this behavior is not known.

These sorption-desorption observations have been reported in detail to illustrate the kind of results obtained and the difficulties encountered. Similar observations were made with a specimen that had previously been outgassed at 100°C. The results are listed in Table 2 in the order in which they were obtained. The data are of limited reliability, especially at the higher temperatures, because of the very small magnitudes of the effects observed. The saturation concentrations are for equilibrium with dioctyl adipate held at room temperature, approximately 25°C.

Ferrocene. Three specimens prepared by sorbing ferrocene into propellant at 100°C gave desorption curves suggesting the presence of water. One of the desorption curves is shown in Figure 14. The first portion of the curve shows the rapid loss of a material presumed to be water. The latter portion of the curve gives a satisfactory determination of the diffusion coefficient of ferrocene. A fourth specimen was stored over Drierite to remove the water. Unfortunately, a portion of the ferrocene was also lost, so that the subsequent desorption experiment gave a less reliable result. The initial rapid weight loss, however, was absent in this case.

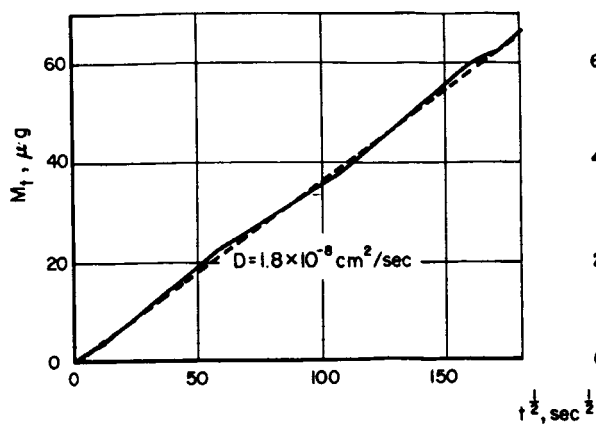


FIGURE 11. SORPTION OF DIOCTYL ADIPATE AT 49.9°C

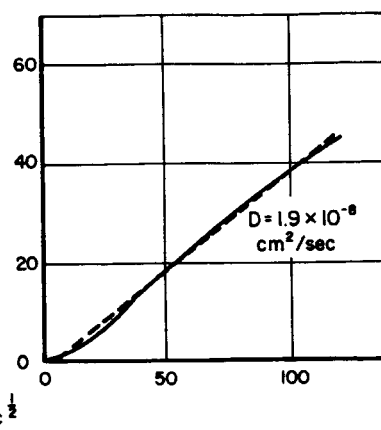


FIGURE 12. DESORPTION OF DIOCTYL ADIPATE AT 50.0°C

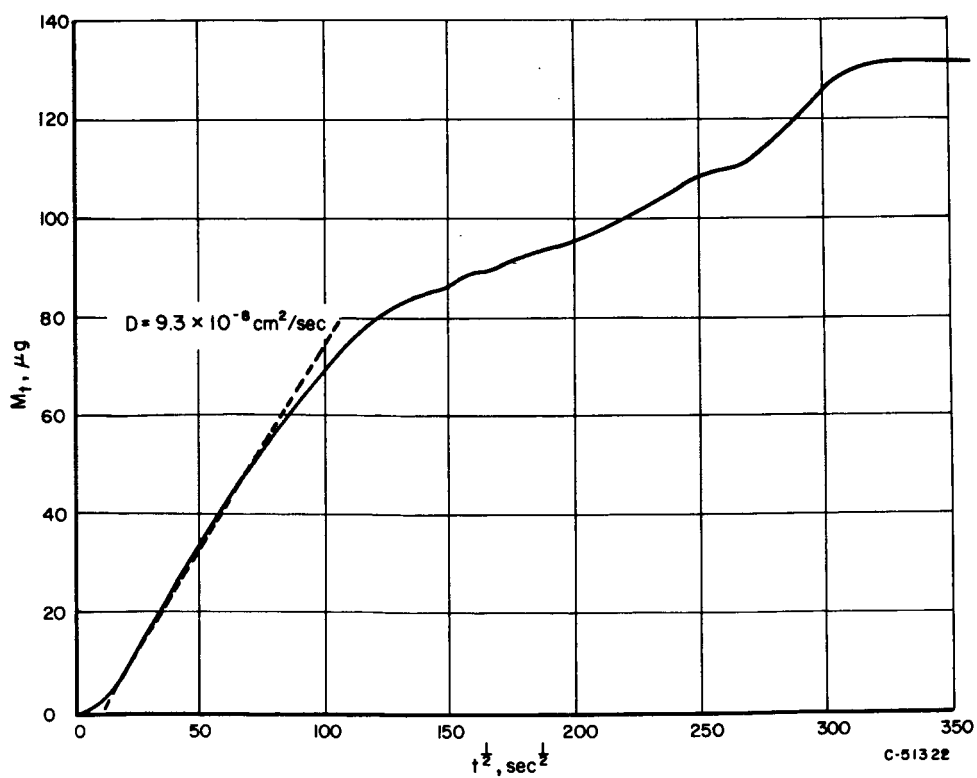


FIGURE 13. SECOND SORPTION OF DIOCTYL ADIPATE AT 50.3°C

TABLE 2. DIFFUSION COEFFICIENT FOR DIOCTYL ADIPATE IN POLYURETHANE PROPELLANT

Specimen Temperature, °C	Sorption or Desorption	Equilibrium Concentration, weight per cent	Approximate D, cm ² /sec
30.0	S	1.8	2.3×10^{-9}
69.2	D	--	4.5×10^{-8}
40.3	S	0.3	1.0×10^{-8}
40.0	D	--	4.8×10^{-9}
50.4	S	0.14	4.0×10^{-8}
68.8	S	0.07	4×10^{-8}
68.7	D	--	7×10^{-8}
69.1	S	0.05	7×10^{-8}
68.5	D	--	1×10^{-7}

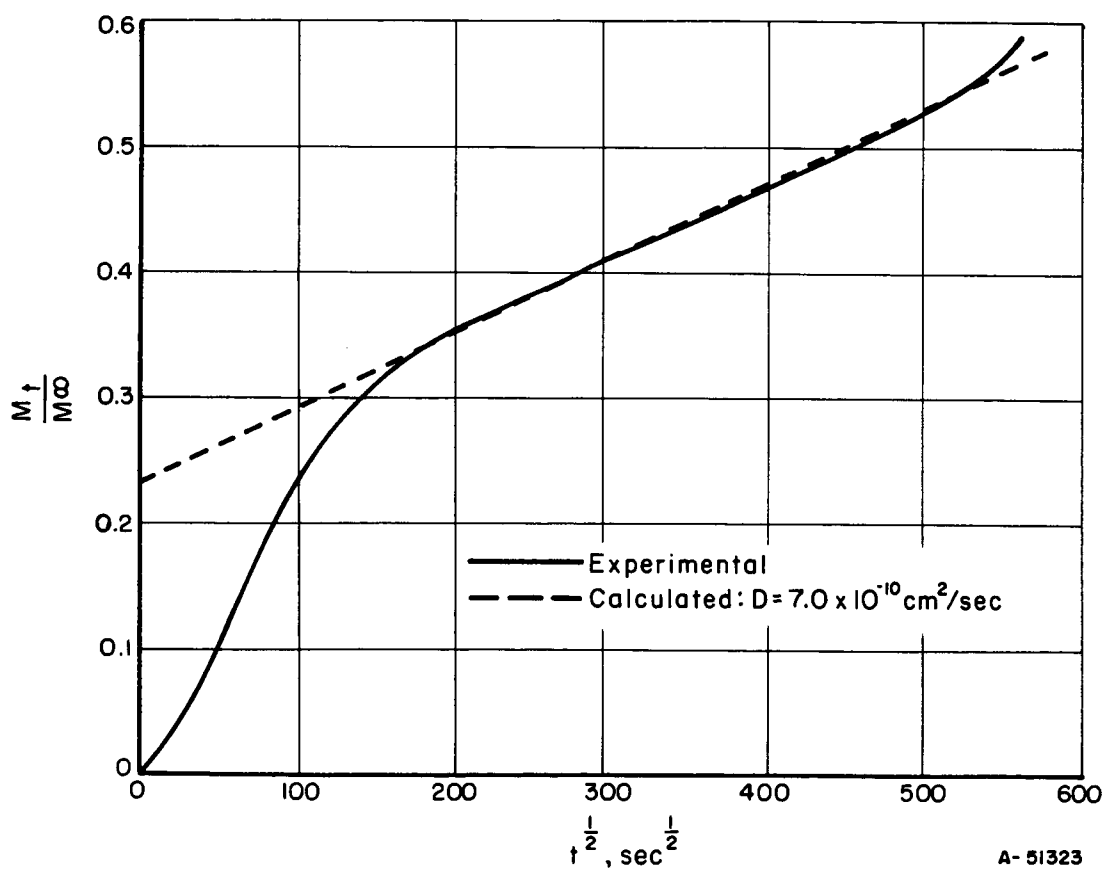


FIGURE 14. DIFFUSION OF FERROCENE FROM FLAT SLAB AT 29.9°C

Several sorption-desorption experiments were conducted in the same manner as for the dioctyl adipate. The first sorption was particularly useful in that it continued for 2 months. The specimen was probably well saturated at the end of that time, so that the subsequent desorption also gave a reliable result. Subsequent sorption experiments were limited in time and gave results of less reliability. All of the results with ferrocene are shown in Table 3. The equilibrium concentrations are for equilibrium with solid ferrocene held at about 25°C.

TABLE 3. DIFFUSION COEFFICIENT FOR FERROCENE IN POLYURETHANE PROPELLANT

Specimen Temperature, °C	Sorption or Desorption	Equilibrium Concentration, weight per cent	D, cm ² /sec
50.2	Desorption after equilibration at 100°C		6.3×10^{-9}
69.2			4.5×10^{-8}
29.9			7.0×10^{-10}
68.1			3×10^{-8}
29.8	S	1.3	1.27×10^{-9}
68.2	D		5.8×10^{-8}
48.7	S	0.6	4×10^{-9}
68.5	D		3.5×10^{-8}
68.5	S	0.08	6×10^{-8}

DISCUSSION OF RESULTS

Vapor Pressure

Vapor pressures for dioctyl adipate and ferrocene agree fairly well with previously stated information and are expressed in the following relationships:

dioctyl adipate

$$\log p \text{ (torr)} = 11.90 - 5397/T$$

ferrocene

$$\log p \text{ (torr)} = 10.96 - 3947/T.$$

The phenyl-beta-naphthylamine data are not as satisfactory or reliable as the above data. Vapor pressures for phenyl-beta-naphthylamine appear to range from 10^{-7} torr at 25°C to 10^{-4} torr at 70°C, the heat of vaporization being approximately 27,000 calories per mole.

Diffusion Coefficient

The diffusion coefficients that are deemed most reliable are summarized in Figure 15. These points all represent desorption runs, and are mostly taken from experiments on specimens previously equilibrated at 100°C. The two results shown for cylindrical samples are seen to agree with those from flat-slab specimens. The diffusion coefficients found for the two additives, ferrocene and dioctyl adipate, are about the same except for the room-temperature results, in which case the diffusion coefficient for dioctyl adipate seems to be somewhat higher than for ferrocene.

One would ordinarily expect a log plot of the diffusion coefficient versus the reciprocal of the temperature to yield a straight line. The data show such a relationship for ferrocene but not for dioctyl adipate. The curvature in Figure 15a is based on only one determination, which appears to be reliable. It is not possible to say with certainty, therefore, that there is any real difference in the results for the two additives.

In Table 4 the results of several previous workers are compared with the results of this research. All values, with the exception of Battelle's, are based on an extrapolation to zero concentration of additive, and all are at 25°C. Extensive extrapolations were required to obtain the polyvinyl chloride results. The diffusion coefficients obtained in this research are close to those found by others for hydrocarbons in polyisobutylene, but differ from those for methacrylate polymers, polyvinyl chloride, and polyvinyl acetate. One expects to find lower diffusion coefficients in highly polar systems, such as in Reference 8.

TABLE 4. COMPARISON OF DIFFUSION COEFFICIENTS AT 25°C

Polymer	Additive	log D	Reference
Polyurethane propellant	Dioctyl adipate	-8.7	This research
Polyurethane propellant	Ferrocene	-9.4	This research
Polyisobutylene	Propane	-8.8	6 and 9
Polyisobutylene	n-Butane	-8.9	9
Polyisobutylene	Isobutane	-9.3	9
Polyisobutylene	n-Pentane	-9.0	9
Polyisobutylene	Isopentane	-9.3	9
Polyisobutylene	Neopentane	-9.7	9
Polyisobutylene	Cetane	-9.0	5
Poly-n-hexyl methacrylate	Cetane	-8.4	5
Poly-n-octyl methacrylate	Cetane	-7.8	5
Poly-n-dodecyl methacrylate	Cetane	-7.6	5
Polyvinyl chloride	Tricresyl phosphate	-10.2(a)	7
Polyvinyl chloride	Dibutyl sebacate	-10.4(a)	7
Polyvinyl chloride	Dibutyl phthalate	-9.9(a)	7
Polyvinyl acetate	Acetone	-12.2(a)	8

(a) Extrapolated from higher temperatures.

The diffusion coefficients have been calculated on the assumption that they are not concentration dependent. Since the concentration range is small, this assumption is approximately correct. The results for dioctyl adipate seem to indicate, however, that higher concentrations give slightly higher results. This is in conformity with the results of others. (5,6,7,8)

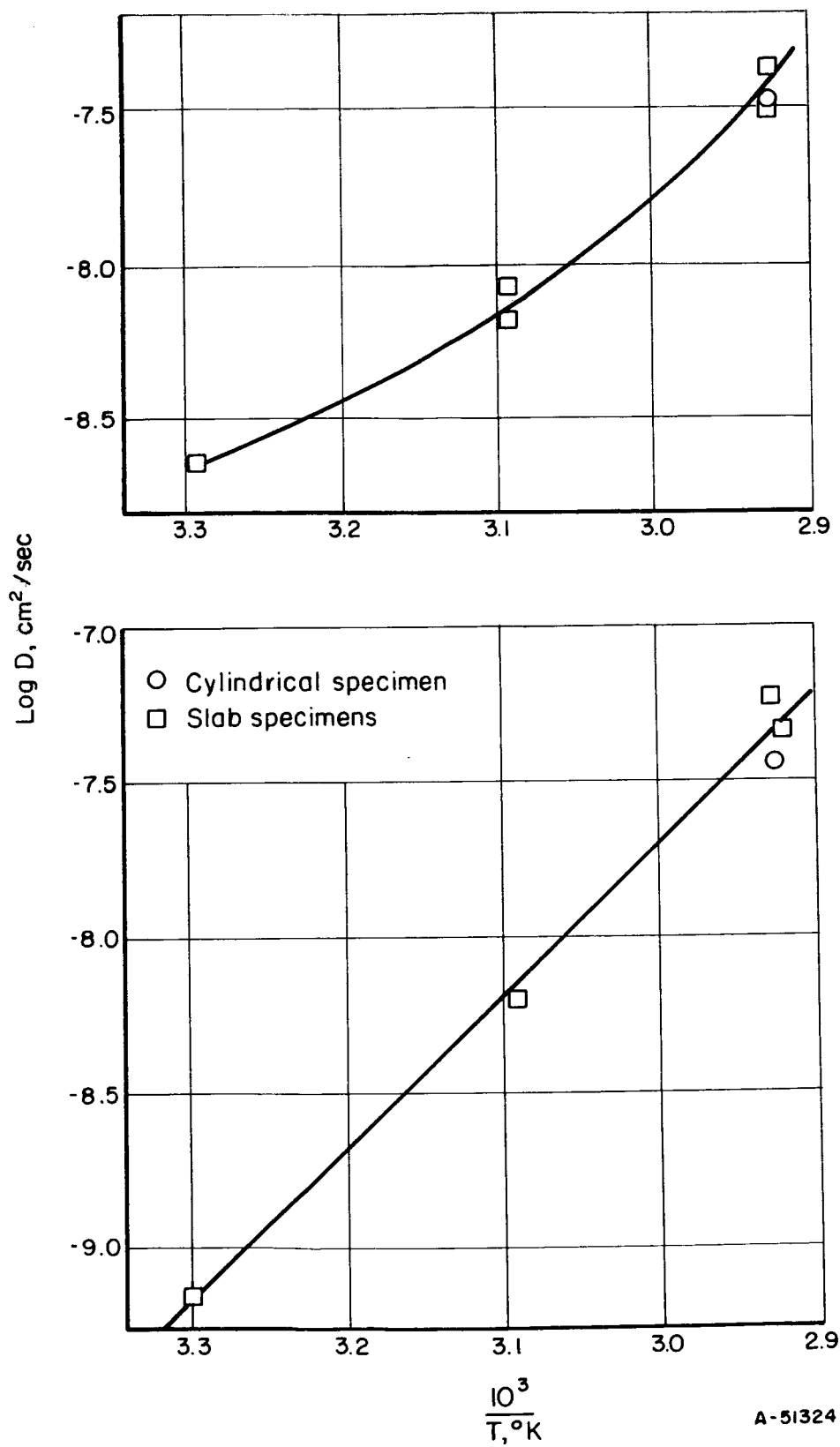


FIGURE 15. DIFFUSION COEFFICIENT FOR DIOCTYL ADIPATE AND FERROCENE IN POLYURETHANE PROPELLANT

The propellant, which is the diffusion medium in this work, has so far been considered as though it were a homogeneous material. Actually, only one-fourth of the material is polymer, the rest being solid inclusions presumably impermeable to the diffusing additives. If diffusion takes place entirely within the polymer phase, one would expect to find diffusion coefficients considerably lower than for a material consisting of the polymer alone. Comparison with results for somewhat similar materials (Table 4) shows that the diffusion coefficients are not lower. A more direct comparison with the pure polymer case would be desirable. Meanwhile, the suggestion must be considered that diffusion takes place through cracks and interphase boundaries, as well as through the bulk polymer phase.

Several rather tentative observations in this work could be explained on the basis of such "structure dependent" diffusion. It would account, first of all, for the relatively high values of the diffusion coefficient, in comparison with similar work on polymer systems. The observed curvature in Figure 19 could be accounted for on this basis, since "structure dependent" diffusion is expected to be less temperature dependent than "volume" diffusion. Such a mechanism would also help to account for some of the scatter in the results with dioctyl adipate, in that mechanical working, temperature cycling, and continued diffusion might tend to loosen the bond between the polymer and solid inclusions, thus opening up diffusion paths. The last four results of Table 2 suggest such a trend. On the other hand, Figures 15a and 15b point to an activation energy of about 20 kcal, which is about as expected for volume diffusion.⁽⁹⁾

It has been noted that the three additives investigated here have about the same diffusion coefficients in the polyurethane propellant. The results are also close to those obtained for butane, pentane, and cetane in polyisobutylene.^(5,6,9) These diffusing substances are all hydrocarbons or similar to hydrocarbons. The diffusion of acetone in polyvinyl acetate is much slower. It seems likely that the additives studied in this program would exhibit diffusion behavior in butadiene-type binders similar to that observed in the polyurethane. More strongly polar molecules may behave differently. These observations are based on limited data, however, and should be subjected to further investigation.

Application to Space Storage

The results obtained in this work, if substantiated and extended to other propellant systems, can be applied to calculate composition changes in propellant grains exposed to the environment of outer space. Such a calculation, to be reasonably accurate, will have to take into account the following complicating factors. In order to solve the diffusion equation with reasonable facility, a simple geometry must be assumed that approximates the more complicated geometry usually used in solid-propellant grains. The pressure of the escaping volatile material will not be zero inside the grain perforation, so that appropriate modifications in the diffusion equation will have to be made. Since the diffusion coefficient is strongly temperature dependent, the average temperature of the propellant grain must be known or assumed.

Some very rough calculations will serve to indicate the magnitude of the loss to be expected. The total loss from a semi-infinite slab per square centimeter of surface is given by

$$M_t = 2C_0 (Dt/\pi)^{1/2} \quad , \quad (10)$$

where C_0 is the initial concentration in g/cm^3 . If one allows that at 30°C , $D = 10^{-9} \text{ cm}^2/\text{sec}$ (for either additive), and calculates the loss for a 1-year period, one finds that

$$M_t/C_0 = 0.2 \text{ cm}.$$

This means that the loss will amount to 1/5 of the additive originally contained in 1 cm^3 . If C_0 is approximately 10^{-2} g/cm^3 , this would be $2 \times 10^{-3} \text{ g/cm}^2$. It can be shown that almost all of the material will come from the $1/2 \text{ cm}$ adjacent to the surface. This is based on the assumption of zero concentration at the surface, and is therefore the maximum amount of additive that can be lost.

This diffusion-limited loss may now be compared with the loss that would take place if the rate were limited by vaporization and effusion rates. The vaporization rate is given by Equation (1). Assuming, for simplicity, that $\alpha = 1$ and that the molecular weight is approximately equal numerically to the absolute temperature, the equation becomes

$$G/At = 5.8 \times 10^{-2} p,$$

where G/At is the loss rate in $\text{g/cm}^2 \text{ sec}$ and p is the effective vapor pressure in torr. At 30°C , the vapor pressure of ferrocene is about 10^{-2} torr and that of dioctyl adipate is about 10^{-6} torr. It will be assumed that the effective vapor pressure of the propellant will be approximately proportional to the concentration of the vaporizing species. For a 1 per cent solution, this will be 10^{-4} for ferrocene and 10^{-8} for dioctyl adipate. Under the most favorable conditions for vaporization, that is, no depletion of the surface layer, this will be the pressure inside the rocket. Now the ratio of throat area to propellant surface area can be assumed, in a typical case, to be about 3×10^{-3} ⁽¹⁾. This will be the area in sq cm through which the vapor from each sq cm of propellant surface will be lost via the nozzle. Substituting these values for A and p , one finds, for t equivalent to 1 year, $G = 0.5 \text{ g/cm}^2$ for ferrocene, and $G = 5 \times 10^{-5} \text{ g/cm}^2$ for dioctyl adipate. These values are for the most favorable case, i. e., no surface depletion. If the process is limited by diffusion, then smaller losses will occur.

Comparison of these values with that previously estimated for the diffusion-limited case is striking. In the case of ferrocene, the process is plainly limited by diffusion. Even if the estimated rate of vaporization and effusion were reduced by a factor of 100 to allow for surface depletion of the propellant with respect to ferrocene, the loss rate would still be high enough to keep up with the diffusion rate. In the case of dioctyl adipate, on the other hand, the loss rate is plainly limited by the rate of effusion through the nozzle. Even if diffusion were so rapid as to keep the surface at its original dioctyl adipate concentration, the effusion rate through the nozzle would be so low that in a year's time only 0.05 mg/cm^2 would be lost (a completely negligible amount). One can conclude, therefore, that under the postulated conditions the loss of either of these materials would not be serious. With a different area ratio or different temperature, of course, the loss would be greater or less.

FUTURE WORK

The first importance of the work presented here and of similar work extended to other propellants and additives is in relation to the possibility of loss of the additive during space storage. As a general conclusion, it seems that, even under the worst

conditions likely to be encountered, the loss through this mechanism will be significant only after very long times in space. Except for exceedingly long missions, it should not be necessary to seal the nozzle to prevent loss of material from the propellant.

Since so few materials actually have been examined, it seems advisable to study the complete propellant before use on extended space-storage missions is attempted. It has been shown here that such a study can be made with relatively short-term experiments. The diffusion coefficients determined in these experiments can then be used to predict reliably the behavior of additives in propellants over a period of years. A "test" of a loaded rocket in a large evacuated chamber for an extended period of time is deemed to be neither necessary nor reliable as an indication of changes in the propellant.

A second application deriving from this study is in the direction of an improved understanding of diffusion in polymers. From the results of this work, and from previous research on polymer systems, it has not been possible to draw general conclusions that would allow the prediction of diffusion coefficients in other solid propellants. An understanding of the diffusion process and a knowledge of diffusion coefficients are important in many aspects of the manufacture and handling of solid propellants. The loss in vacuum is also of great importance in other polymers used in space applications. It would therefore be profitable to extend the studies to binder-additive systems without solid inclusions, and to other polymers and other additives.

CONCLUSIONS

- (1) Vapor pressures have been determined in the range 10^{-3} to 10^{-7} torr for bis(2-ethyl-hexyl) adipate (or dioctyl adipate), ferrocene, and phenyl-beta-naphthylamine.
- (2) Diffusion coefficients in the range 30 to 70°C have been determined for dioctyl adipate and ferrocene in a polyurethane propellant. The results were nearly the same in the two cases and were somewhat higher, but in the same range, as previously reported diffusion coefficients for hydrocarbons in polymers.
- (3) The primary transport mechanism seems to be volume diffusion through the polymer phase, though there is some evidence of structure-dependent interphase diffusion in addition.
- (4) In a typical rocket at about 30°C, the diffusion-limited loss in 1 year could amount to about 2 mg/cm² of propellant surface. Only the propellant within about 1/2 cm of the surface would be appreciably affected. For additives of low vapor pressure, the loss would be less, and would be limited by the rate of effusion through the rocket nozzle.
- (5) For limited periods in space, say 1 to 2 years, the loss of additives from solid-propellant grains should not jeopardize the designed rheological or combustion properties of the propellants.

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The data upon which this report is based are recorded in Battelle Laboratory Record Books Nos. 21453 and 22178.

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